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ELECTRICAL AND MAGNETIC CHARACTERISTICS OF IRON-CONTAINING GLASS IN CRYSTALLIZATION

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The effect of heat treatment on the phase composition, microstructure, and properties of glass ceramics is studied. The possibility of obtaining glass ceramic materials of virtually the same composition with a wide range of electromagnetic characteristics on the basis of iron-bearing glass is demonstrated.

Iron-bearing oxide glasses with $\text{Fe}_x\text{O}_y \geq 15\%$ are prone to volume crystallization. They can be used to produce glass ceramics with low resistivity and magnetic characteristics without introducing additional catalytic additives. In this case iron oxides act as initiators of the process of transformation of glass into glass ceramics. At the same time, they contribute to preparing the glass matrix for electric transfer. However, the mechanism of the formation of the main crystalline phases and the residual vitreous phase responsible for the type of conduction and the end properties of the material has not been deeply investigated.

In this context, in order to produce glass ceramic materials with preset electromagnetic properties, the process of crystallization of iron-bearing glasses and its effect on volume resistivity ρ_V , magnetic susceptibility χ , and structural and phase modifications occurring under heat treatment was investigated.

A series of glasses was investigated (here and elsewhere wt. %): 40–60 SiO_2 , 10–15 CaO , 2–5 Al_2O_3 , 10–15

MgO , 5–10 R_2O , 5–35 Fe_xO_y , whose compositions converted to a ternary composition in the $\text{CaO} - \text{Fe}_2\text{O}_3 - \text{SiO}_2$ system are located within the ranges of cristobalite (182–184 and 189–191), hematite (193), and metasilicate (185–188 and 192) (Fig. 1).

The glasses were synthesized using iron-containing waste from the Kursk Magnetic Anomaly (crystalline schist and waste from concentration of ferrous quartzite, i.e., tails), in which the ratio between the oxidized and the reduced forms of iron was equal to 0.69 and remained virtually constant in melting in a laboratory furnace with carborundum heaters (air atmosphere). The production of glasses (technology of melt preparation), their machine treatment, application of electrodes, and measurements of electromagnetic characteristics were carried out according to the known methods [1].

It was found that $\log \rho_V$ of the samples varied from 6.7 to 9.2. Glass composition 189 containing about 32% Fe_xO_y and having one of the lowest values of resistivity ($9.3 \times 10^{-9} \Omega \cdot \text{m}^{-1}$) was selected from the considered glass series to produce glass ceramics. This choice was eco-

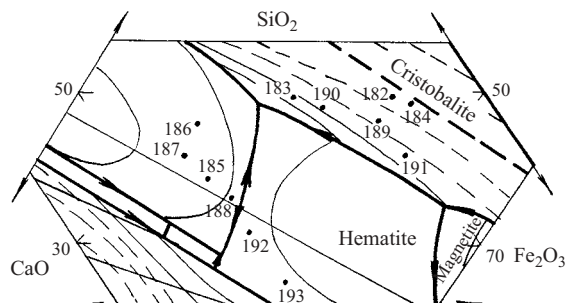


Fig. 1. Location of figurative points of iron-containing compositions on a fragment of the phase diagram of $\text{CaO} - \text{Fe}_2\text{O}_3 - \text{SiO}_2$ system.

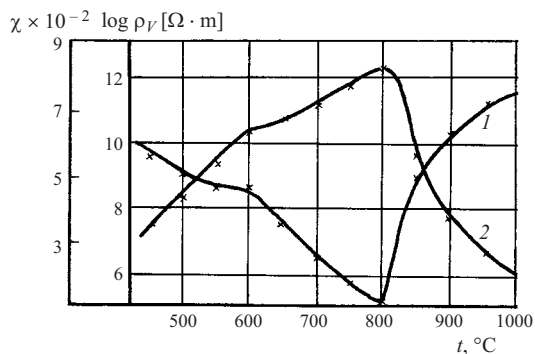


Fig. 2. Temperature dependence of resistivity logarithm $\log \rho_V$ (1) and magnetic susceptibility χ (2) of devitrifying glass 189.

nomically justified (the maximum use of schist and tailings in the glass batch was 58.7%). However, glass 189 in heat treatment exhibited complex variations of temperature dependences $\log \rho_V$ and χ (Fig. 2): curve 1 exhibited a break in the vicinity of 600°C and a minimum at 800°C, which coincided with a smooth transition and a maximum in curve 2 at the same temperatures.

Judging from the x-ray phase analysis and the electron microscope data (Fig. 3), these variation of $\log \rho_V$ and χ correlate to different compositions and types of crystalline phases that are formed in low-temperature (800°C) and high-temperature (950°C) treatment of glass. There are liquation areas, i.e., drops of size 300–1200 nm in the initial glass structure (Fig. 3a). It is possible to identify single sites (about 150 nm) of originating crystalline phases in the vitreous matrix surrounding the drops. As the heat treatment temperature increases to 700°C, the amount of the microcrystalline phase increases. However, the size of crystals grows only within the matrix glass, not affecting the drops (Fig. 3b and c). Treatment of samples in 40% HF indicates that the vitreous phase of the drops is less susceptible to pickling than the surrounding phase [2]. This suggests that the drops mainly represent the silicate phase, whereas the matrix is enriched with iron oxides.

It can be seen in Fig. 3d that the matrix glass becomes fully crystallized, as a result of heat treatment at 800°C. The glass ceramic material with conductivity of about $10^{-5} \Omega \cdot m$ consists of the vitreous phase in the form of areas with the lateral section (1400 nm) and the fine-grained crystalline phase identified as magnetite ($d/n = 2.56, 2.97, 1.62$, and 1.48 \AA) based on the presence of so-called nine lines in the NGR spectra [3] and the ASTM database. After heat treatment at 850–950°C, the crystallization product is a glass ceramic as well (Fig. 3e and f), but its degree of magnetization decreases perceptibly. The crystalline phase formed in this case differs in its structure from the low-temperature phase and represents pyroxene, mainly of the diopside-hedenbergite composition ($d/n = 2.99, 2.51, 2.54, 1.67 \text{ \AA}$ and $d/n = 3.01, 2.52, 2.56 \text{ \AA}$). The considered composition is positioned near the SiO_2 – pyroxene boundary in the $\text{CaO} - \text{MgO} - \text{SiO}_2$ phase diagram.

The results of the x-ray-phase analysis studies (Fig. 3, curves 1 and 2) suggested the following interpretation of the phenomena observed.

Up to a temperature of 700°C, the crystallization in the matrix glass proceeded due to iron oxides acting as the crystallization catalysts. The coexisting vitreous phase in the form of drops was non-conducting and the crystalline phase

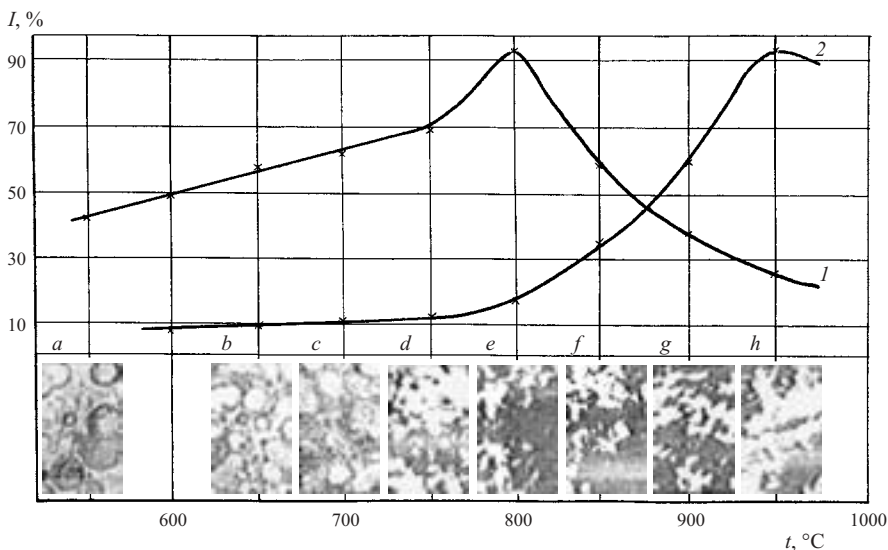


Fig. 3. Formation of crystalline phases in the structure of heat-treated iron-bearing glass. Electron microscope photos ($\times 600$) of: a) initial glass; b, c, d, e, f, g, and h) glass crystallized at temperatures of 650, 700, 750, 800, 850, 900, and 950°C, respectively; 1) Fe_3O_4 ; 2) pyroxene solid solutions.

(Fe_3O_4) emerging from the matrix was responsible for increased conductivity and magnetic susceptibility. The maximum parameters of ρ_V and χ were registered at a temperature of 800°C, which coincided with the temperature of the maximum formation of magnetite, which is the electron donor in the scheme $\text{Fe}_6^{3+} \rightleftharpoons \text{Fe}_6^{2+}$. This was facilitated by the relatively low temperature of synthesis (1250°C), the exposure of the melt for 3 h, and using batch materials with a total $\text{Fe}_2\text{O}_3 : \text{FeO}$ ratio equal to 21 : 11. A comparison of the surface areas of the doublets of bi- and trivalent iron in the NGR spectra with coordination 6 for the sample heat-treated at 800°C indicated that an $\text{Fe}_2\text{O}_3 : \text{FeO}$ ratio approximately equal to 2 : 1 persisted. The increase in ρ_V and the decrease in χ at the high-temperature stage of material treatment can

TABLE 1

Heat treatment, °C	Glass properties				
	microhardness, MPa	density, kg/m ³	heat resistance, °C	water resistance, hydrolytic class	abrasive resistance, 10^{-3} kg/m^2
Initial glass	3450	2615	94.2	3	0.61
500	—	2625	93.2	3	—
550	—	2650	127.4	3	—
600	—	2670	211.6	3	—
650	—	2690	133.0	3	—
700	—	2730	151.9	3	—
750	—	2960	178.2	3	—
800	6410	2950	187.1	3	0.047
850	—	3110	205.3	3–2	—
900	—	3200	219.6	2	—
950	7718	3290	227.3	2–1	0.008

be attributed to mutual penetration of crystalline phases Fe_3O_4 , CaMgSiO_6 , and $\text{CaFeSi}_2\text{O}_6$, which have different conducting capacity, and subsequent formation of complex non-magnetic solid solutions of the pyroxene class.

The studies of properties of the initial glass and the products of its devitrification indicated the possibility of obtaining glass ceramics based on iron-containing glass of virtually the same composition under different heat-treatment conditions. The physicochemical properties of the iron-containing glass and the products of its devitrification are listed in Table 1.

The glass ceramic material produced under low-temperature (800°C) heat treatment is conducting ($4.1 \times 10^{-5} \Omega \cdot \text{m}^{-1}$) and can be used in semiconductor engineering. Due to its high magnetic susceptibility, it can be used as a filler in composites absorbing high-frequency magnetic radiation [4] and as tiles for heated floors of industrial premises [5].

The glass ceramic material obtained according to the high-temperature technology has dielectric properties, wear resistance, and chemical and heat resistance, which makes it

suitable for use in household electric equipment and in civil engineering (pipes, slabs, curb stone, cornices, plinths, heat and sound insulation, lining for chutes, trays, bunkers, platforms, etc.)

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